

# Thiol-Terminated Di-, Tri-, and Tetraethylene Oxide Functionalized Gold Nanoparticles: A Water-Soluble, Charge-Neutral Cluster

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A series of gold nanoclusters stabilized by ligands containing short ethylene oxide oligomers of fixed length were prepared and characterized. The thiols  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{SH}$  (where  $n = 2, 3$ , and  $4$ ) were substituted onto the surface of 1.8-nm hexanethiol-capped gold clusters by a thiol-exchange reaction, and the resulting nanoclusters were characterized by NMR, FTIR, and UV/vis spectroscopies; TGA; and TEM analysis. A degree of ligand exchange greater than 99% was achieved, and the gold core diameter remained unchanged in the final material. Of particular interest, the cluster with  $n = 2$  was water-insoluble, whereas those with  $n = 3$  or  $4$  were water-soluble. The thin-film electrical conductivities of these clusters were compared with those of alkanethiol-capped clusters of similar chain lengths and found to be roughly 1 order of magnitude greater. In a chemical vapor sensor configuration, this series of clusters displayed strong electrical responses that showed a correlation between the length of the ethylene oxide ligand and the polarity of the vapor.

## Introduction

Gold nanoclusters have received significant attention recently as potential building blocks for nanoelectronics.<sup>1</sup> One example of an area in which an opportunity is seen for these nanoclusters to make an impact is that of chemical sensors, owing to the ease of fabrication of such devices, and several examples of nanocluster-based sensors have already been reported.<sup>2,3</sup> Many of these studies utilize alkanethiol-stabilized clusters prepared by the method of Brust et al.,<sup>4</sup> which are readily synthesized in a variety of core and shell sizes, are stable and charge-neutral, and are able to undergo thiol substitution reactions that facilitate their self-assembly into nanostructures. Despite these advantages, the solubility of such clusters is limited to organic solvents, and it is not difficult to envision situations in which aqueous solubility is required. In this work, we report a new type of gold nanocluster that can be viewed as the complement of the alkanethiol cluster, retaining almost all of its desirable properties while incorporating water solubility.

Most work in the literature involving aqueous gold clusters uses the well-known citrate-stabilized gold colloids.<sup>5</sup> These clusters utilize ionic interactions on the

cluster surface to obtain solubility, and as a result, they agglomerate irreversibly on removal of the solvent. They are also larger in size ( $\sim 12$  nm) than the typical alkanethiol-stabilized cluster ( $< 2$  nm). Surprisingly, reports of water-soluble thiol-coated gold nanoparticles are limited,<sup>6–16</sup> and most of these clusters are stabilized by an alkanethiol terminating in either an ionic species<sup>6,7,16</sup> or a carboxylic acid group.<sup>9–11,13,14</sup> The aqueous solubility of these clusters is often coupled to the pH of the solution,<sup>8,15</sup> and the presence of functional groups that can participate in hydrogen bonding between clusters can lead to particle agglomeration.<sup>13</sup> Additionally, the presence of ions in the system leads to interference during conductivity measurements and electron-transport studies.<sup>17</sup> Ionic effects are of particular concern in nanoelectronics applications, where they can accentuate threshold nonuniformities associated with

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background charges.<sup>18</sup> An interesting example of a charge-neutral, nonionizable water-soluble cluster was reported by Wuelfing et al., who attached a poly(ethylene glycol) chain to the surface of a gold nanocluster.<sup>12</sup> Although this cluster exhibits the desired solubility properties, the extreme size of the ligand (a polymer of MW 5000) results in an inability for this cluster to undergo thiol-exchange reactions. This is a serious drawback as such reactions are required to perform the self-assembly of clusters onto surfaces and devices, a necessary step in the further study of these materials as nanoscale building blocks.

Herein, we report the synthesis and characterization of water-soluble gold nanoclusters that, like the alkanethiol-stabilized clusters, are easily prepared, small in core size, stable, charge-neutral, and able to undergo thiol-exchange reactions. These clusters are capped by thiols containing short ethylene oxide chains,  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{SH}$  (where  $n = 2, 3$ , and  $4$ ). In addition, the potential utility of such clusters is demonstrated by their incorporation into a metal–insulator–metal ensemble (MIME) chemical vapor sensor<sup>2</sup> as a water-vapor-responsive coating. We expect these clusters to also have important implications for nanostructure fabrication in aqueous environments, e.g., in DNA-based assembly.<sup>19</sup>

## Experimental Section

**General Considerations.** All solvents were used as received from commercial sources.  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OH}$  was purchased from Aldrich and used as received. In accordance with previous conventions,<sup>20</sup> the following abbreviations are used to describe the gold nanoclusters: alkane clusters are designated as  $\text{AuC}_n(X:Y)$ , where  $n$  is the number of carbon atoms in the thiol chain and  $X$  and  $Y$  are the molar equivalents of  $\text{AuCl}_4^-$  and thiol, respectively, used in the preparation. The  $\text{AuC}_6(1:1)$  cluster was prepared<sup>21</sup> using a method very similar to the general procedure reported by Brust et al.<sup>4</sup> The ethylene oxide oligomer-capped clusters are denoted as  $\text{AuEO}_2$ ,  $\text{AuEO}_3$ , or  $\text{AuEO}_4$  depending on the number of  $-\text{OCH}_2\text{CH}_2-$  repeat units present in the ethyleneoxy backbone. FTIR spectra were obtained on a Nicolet Magna 750 FTIR spectrometer by evaporating several drops of a  $\text{CHCl}_3$ /cluster solution on a  $\text{NaCl}$  plate.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained on a Bruker AC-300 instrument operating at 300.13 and 75.468 MHz, respectively. Spectra were referenced to TMS using the residual proton and carbon signal of  $\text{CDCl}_3$  at  $\delta$  7.24 and 77.0, respectively. Thermal gravimetric analysis (TGA) was performed under a  $\text{N}_2$  flow on a DuPont Instruments model 951 thermogravimetric analyzer with a 10 °C/min heating rate to a final temperature of 600 °C. UV/vis data were obtained on a Perkin-Elmer Lambda 5 spectrophotometer using solution concentrations of approximately 0.1 mg/mL. Transmission electron microscopy (TEM) images were obtained on a Hitachi H9000-UHR instrument operating at 300 kV, with samples prepared by depositing nanoparticles from solution onto the edge of a cleaved silicon wafer.

**Preparation of  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{SH}$  ( $n = 2, 3, 4$ ).** A similar reaction scheme was used to prepare all three ligands. A sample procedure for  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{SH}$  is as follows:  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OH}$  (10.0 g, 60.9 mmol) was dissolved in 12 mL of pyridine and cooled to 0 °C. *p*-Toluenesulfonyl chloride

(11.6 g, 60.9 mmol) dissolved in 12 mL of pyridine was added dropwise under  $\text{N}_2$ . The reaction was stirred for 2.5 h, at which point the flask was sealed and stored at 2 °C overnight. This mixture was then added to 120 mL of ice water and stirred for 1 h. Extraction of this solution with  $\text{CH}_2\text{Cl}_2$  permitted isolation of the tosylate as an oil. It was immediately dissolved in a minimum amount of EtOH and transferred to a flask, to which thiourea (4.64 g, 60.9 mmol) dissolved in 15 mL of  $\text{H}_2\text{O}$  was then added. The reactants were refluxed for 2 h. NaOH (2.68 g, 67.0 mmol) in  $\text{H}_2\text{O}$  was then added, and reflux was maintained for 1.5 h. The solution was cooled to room temperature, concentrated, and neutralized with HCl. The product was extracted from this aqueous solution with  $\text{CH}_2\text{Cl}_2$  and isolated as a yellow oil that was purified by vacuum distillation (60 °C, 1 Torr), producing 3.46 g of thiol (32% overall yield).  $^1\text{H}$  NMR:  $\delta$  1.56 (t, 1H,  $-\text{SH}$ ), 2.67 (q, 2H,  $-\text{CH}_2\text{SH}$ ), 3.36 (s, 3H,  $\text{CH}_3-$ ), 3.56 (multiplet, 12H, methylene groups in backbone).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  24.2 (s,  $-\text{CH}_2\text{SH}$ ), 59.0 (s,  $\text{CH}_3-$ ), 70.4 (s,  $-\text{OCH}_2\text{CH}_2-$ ), 70.5 (s,  $-\text{OCH}_2\text{CH}_2-$ ), 72.0 (s,  $-\text{OCH}_2\text{CH}_2-$ ), 72.8 (s,  $-\text{OCH}_2\text{CH}_2-$ ). FTIR (cm<sup>-1</sup>): 2871 (s), 2549 (w), 1112 (s). GC/MS (EI): 181 (M + 1). Additional details of the synthesis and characterization of these ligands are reported elsewhere.<sup>22</sup>

**Preparation of  $\text{AuEO}_2$ ,  $\text{AuEO}_3$ , and  $\text{AuEO}_4$  Clusters.** Similar procedures were used to prepare the  $\text{AuEO}_2$ ,  $\text{AuEO}_3$ , and  $\text{AuEO}_4$  clusters. A sample procedure for  $\text{AuEO}_3$  is as follows:  $\text{AuC}_6(1:1)$  [0.180 g, corresponding to approximately 0.3 mmol of  $\text{CH}_3(\text{CH}_2)_5\text{SH}$  on the surface of the cluster] was added to a 20-mL vial equipped with a stir bar, and the solid was dissolved in 1–2 mL of  $\text{CH}_2\text{Cl}_2$ , forming a dark solution.  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{SH}$  (0.165 g, 0.92 mmol) was added via pipet, and the solution was stirred at room temperature for 7 h. The solvent was evaporated, leaving a dark solid and a few drops of liquid. An IR spectrum was recorded for this solid material to check the progress of the reaction, after which the solid was redissolved in  $\text{CH}_2\text{Cl}_2$ , and an additional 0.165 g of  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{SH}$  added, followed by stirring for 7 h. The solution was rotovapped to dryness, and the resulting dark solid was washed with approximately 25 mL of heptane, divided into several portions. This material was again examined by FTIR spectroscopy. The washed solid was dried under vacuum for 5 h, yielding 0.151 g of  $\text{AuEO}_3$ . By integration of the  $\text{AuEO}_3$  and residual  $\text{AuC}_6(1:1)$  peaks in the  $^1\text{H}$  NMR spectrum of the final product, the degree of exchange was estimated to be >99%.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the  $\text{AuEO}_2$ ,  $\text{AuEO}_3$ , and  $\text{AuEO}_4$  clusters all exhibited extremely broad peaks with positions that corresponded well to the appropriate free thiols. In all three cases, the  $\text{HS}-$  and  $\text{HSCH}_2-$  protons were not visible. A small triplet present at approximately  $\delta$  2.8 in all samples was attributed to the corresponding ethylene oxide disulfide and could be removed by dialysis overnight.  $\text{AuEO}_2$   $^1\text{H}$  NMR:  $\delta$  3.37 (br, terminal  $-\text{CH}_3$ ), 3.53 (br, methylene protons).  $\text{AuEO}_2$   $^{13}\text{C}$  NMR:  $\delta$  58.99 (br, terminal  $-\text{CH}_3$ ), 70.29 (br, methylene groups), 71.91 (br, methylene groups).  $\text{AuEO}_3$   $^1\text{H}$  NMR:  $\delta$  3.36 (br, terminal  $-\text{CH}_3$ ), 3.63 (br, methylene protons).  $\text{AuEO}_3$   $^{13}\text{C}$  NMR:  $\delta$  59.04 (br, terminal  $-\text{CH}_3$ ), 70.57 (br, methylene groups), 71.95 (br, methylene groups).  $\text{AuEO}_4$   $^1\text{H}$  NMR:  $\delta$  3.36 (br, terminal  $-\text{CH}_3$ ), 3.62 (br, methylene protons).  $\text{AuEO}_4$   $^{13}\text{C}$  NMR:  $\delta$  59.01 (br, terminal  $-\text{CH}_3$ ), 70.53 (br, methylene groups), 71.93 (br, methylene groups). Similarly, FTIR spectra of  $\text{AuEO}_2$ ,  $\text{AuEO}_3$ , and  $\text{AuEO}_4$  were very similar to those of the free thiols, and the S–H stretch (occurring at approximately 2550 cm<sup>-1</sup> in the free thiols) was not visible for any of the cluster samples.  $\text{AuEO}_2$  IR (cm<sup>-1</sup>): 2870, 1080.  $\text{AuEO}_3$  IR (cm<sup>-1</sup>): 2860, 1100.  $\text{AuEO}_4$  IR (cm<sup>-1</sup>): 2860, 1105.

**UV/Vis Cluster Stability Experiment.** Three different solutions were prepared: 0.1 mg/mL  $\text{AuEO}_3$  in 1 M HCl, 0.1 mg/mL  $\text{AuEO}_3$  in triply distilled  $\text{H}_2\text{O}$ , and 0.05 mg/mL  $\text{AuEO}_3$  in 0.5 M NaOH. A spectrum was recorded for each solution immediately upon mixing and then after 1 h, 6 h, 1 day, 5 days, 7 days, 11 days, 2 weeks, 3 weeks, and 5 weeks.

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**AuEO3/Thiol NMR Exchange Experiment.** AuEO3 (0.023 g, corresponding to approximately 0.03 mmol of thiol) was dissolved in 0.5 mL of  $\text{CDCl}_3$  and added to an NMR tube.  $\text{CH}_3(\text{CH}_2)_7\text{SH}$  (0.005 g, 0.03 mmol) was dissolved in 0.25 mL of  $\text{CDCl}_3$  and added to the tube. A spectrum was recorded immediately after addition and then after the following intervals: 30 min, 3 h, 6 h, 24 h, and 48 h. Spectra were then collected approximately every 3 days. The experiment was terminated after 20 days, when very little change was observed from the previous spectrum.

**Cluster Electrical Conductivity Measurements.** Conductivity measurements were made using an interdigital electrode (Microsensor Systems, Inc.; P/N 302) consisting of 50 finger pairs (15- $\mu\text{m}$  spacing, 15- $\mu\text{m}$  finger width, 4800- $\mu\text{m}$  overlap length, 1500- $\text{\AA}$  electrode thickness) fabricated in gold on a quartz substrate ( $7 \times 12.5 \times 1$  mm). A film of clusters was deposited from a 10 mg/mL solution onto the interdigital electrode by an airbrush technique.<sup>2</sup> The mass of the film was determined after the conductivity measurement by dissolution of the clusters in  $\text{CHCl}_3$  and an analytical absorbance measurement at the plasmon wavelength (507 nm). The film thickness was calculated from the mass of the cluster film, the electrode substrate dimensions ( $1.24 \times 0.74$  cm), and the cluster density ( $\sim 3.2$  g/cm<sup>3</sup>), along with the assumption of a uniform film thickness. A typical calculated film thickness was 0.16  $\mu\text{m}$ . Current-voltage plots were linear over a range from -2.0 to 2.0 V, and the bulk conductivity was calculated from the slope of the  $I$ - $V$  plot according to the following relation for the interdigital electrode<sup>20,23</sup>

$$\sigma = \left[ \frac{d}{(2n-1)L} \right] \left[ \frac{1}{h} \right] \left[ \frac{I}{V} \right]$$

where  $h$  is the film thickness,  $I/V$  is the slope of the current-voltage plot,  $n$  is the number of finger pairs on the electrode,  $d$  is the spacing between finger pairs, and  $L$  is the overlap length of the finger pairs.

**Vapor-Response Measurements.** Electrodes were prepared as described above, and mounted in a custom-designed chamber connected to a computer-controlled vapor generator (Microsensor Systems Inc., model VG7000). The setup was identical to that previously described for the testing of MIME chemiresistor sensors.<sup>2</sup> Vapors of toluene, 1-propanol, and water were generated from bubblers held at 15 °C, diluted to the appropriate concentration using dry air, and delivered to the cluster-coated substrates.

## Results and Discussion

The ethylene oxide stabilized clusters were prepared using a thiol substitution reaction between the free thiols  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{SH}$  ( $n = 2, 3, 4$ ) and the alkane-capped cluster AuC6(1:1). These latter clusters were prepared using a method based on the two-phase solution synthesis<sup>4</sup> reported by Brust et. al. and were isolated and characterized independently prior to the substitution reaction. These alkane-stabilized clusters have been characterized previously,<sup>4,24</sup> and therefore, by using this substitution method, the purity of the final substituted product could be maximized. The tetraoctylammonium bromide used as the phase-transfer catalyst in the two-phase preparation can be effectively

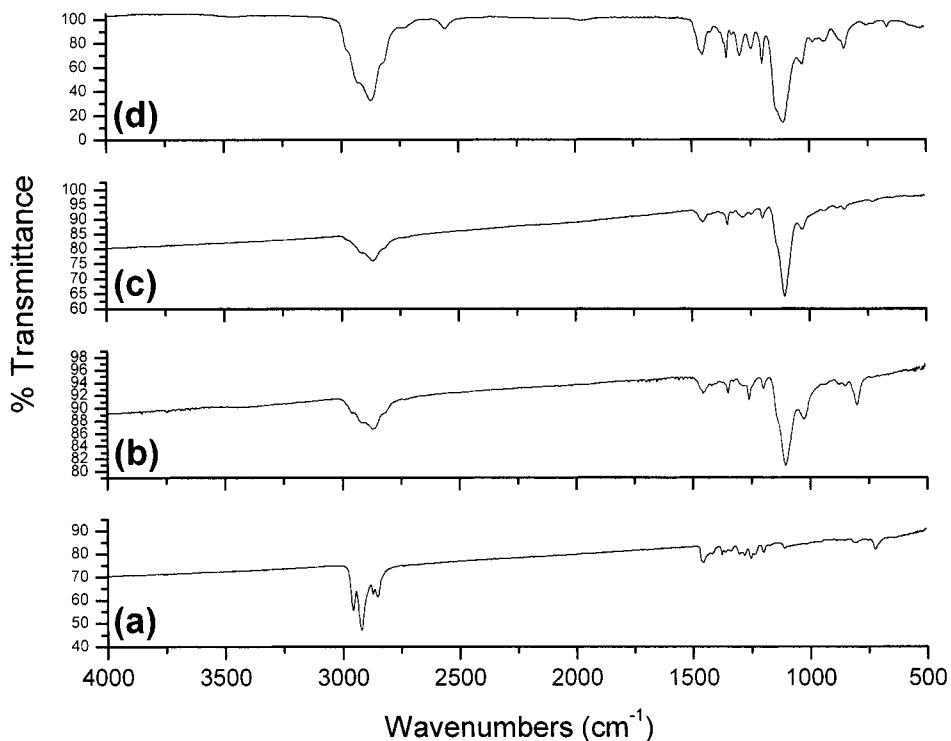
removed following the synthesis of the alkane clusters, but in our experience, this is not always the case when an alternative thiol is used in the reaction. Thiol substitution onto the purified alkane cluster ensures that this organic electrolyte is not present during the subsequent conductivity measurements. A two-step exchange was used for this substitution reaction, wherein the longer ethylene oxide thiol was present in the solution in excess. It is worth noting that the AuEO2 cluster was prepared initially from a three-step substitution reaction, whereas AuEO4 was obtained using the two-step procedure. AuEO3 was isolated from both two- and three-step procedures, and no difference between the two products could be detected. This exchange reaction is known to occur at a reduced rate for longer-chain thiols;<sup>25</sup> therefore, the kinetics favor the formation of the ethylene oxide capped cluster by slowing the reverse exchange after the desired ethylene oxide thiol is substituted onto the gold core. The hexanethiol released from the surface is then removed during the workup, and a fresh solution of the ethylene oxide thiol added. The second stage of the reaction occurs similarly to the first, with the equilibrium again resulting in the preferential removal of the remaining hexanethiol. This results in >99% substitution of the ethylene oxide ligands onto the surface of the cluster, as estimated by a comparison of the integration values for all peaks associated with the product and starting materials in the <sup>1</sup>H NMR spectrum. Also important is the observation that the AuEO3 and AuEO4 clusters do not become water-soluble until after the second stage of the reaction, indicating that both steps are necessary for a complete substitution. Figure 1 shows a comparison of FTIR spectra taken at each stage of the reaction used to prepare AuEO3, and a progression from the AuC6(1:1) cluster to the final product is seen. The final AuEO3 cluster spectrum corresponds well with that of pure  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{SH}$ , and the S-H stretch occurring at 2549 cm<sup>-1</sup> in the pure thiol disappears, as would be expected for binding to the gold surface. In addition, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the AuEO2, AuEO3, and AuEO4 clusters all exhibit broad signals with peak positions that are very similar to those of their corresponding free thiols.

In addition to the purity considerations mentioned above, this exchange method has the added advantage of allowing the selection of a specific gold core size for the clusters prior to reaction. To be sure that this is indeed the case, it is necessary to rule out the possibility that the gold cores fuse into larger sizes during the preparation. A comparison of UV/vis spectra for the three ethylene oxide clusters and the AuC6(1:1) starting material showed four extremely broad and weak surface plasmon peaks at approximately 507 nm, which were essentially identical for all four samples. This indicates that the size of the gold core is preserved in the product, as any increase in core size would manifest itself as a sharper plasmon peak.<sup>24a</sup> Figure 2 shows TEM images of both the AuC6(1:1) and AuEO3 clusters that are consistent with the UV/vis data. The average core size of the AuEO3 clusters shown in Figure 2b is  $2.0 \pm 0.8$  nm (36 particles measured), which is nearly identical

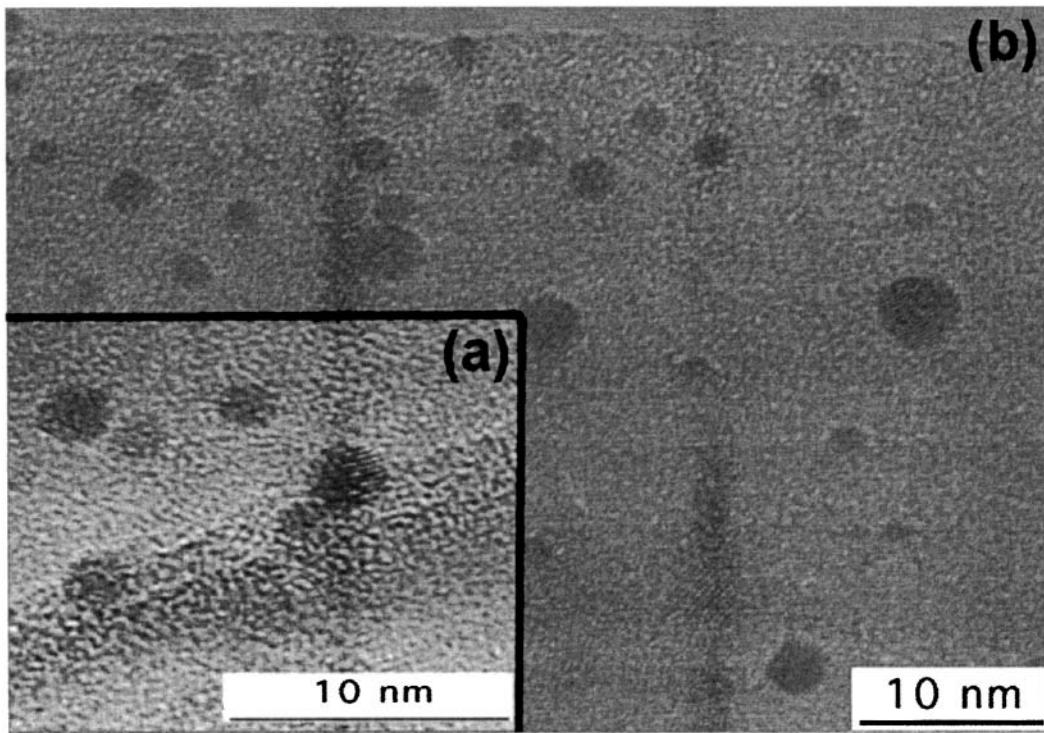
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**Figure 1.** FTIR data for the AuC<sub>6</sub>(1:1)/EO<sub>3</sub>SH exchange reaction: (a) pure AuC<sub>6</sub>(1:1), (b) after 7 h of stirring at room temperature, (c) AuEO<sub>3</sub> final product after the second 7-h reaction, (d) pure EO<sub>3</sub>SH.



**Figure 2.** TEM images of the gold nanoclusters: (a) AuC<sub>6</sub>(1:1) clusters deposited from a heptane solution, average size  $1.8 \pm 0.5$  nm; (b) AuEO<sub>3</sub> clusters deposited from an aqueous solution, average size  $2.0 \pm 0.8$  nm.

to the average core size of  $1.8 \pm 0.5$  nm (22 particles measured) for the AuC<sub>6</sub>(1:1) clusters shown in Figure 2a.

The series of three clusters was also examined using thermal gravimetric analysis (TGA), and the results are summarized in Table 1. The profile of each TGA trace listed in the table showed a single-step weight loss occurring at the reported temperature. Consistent with

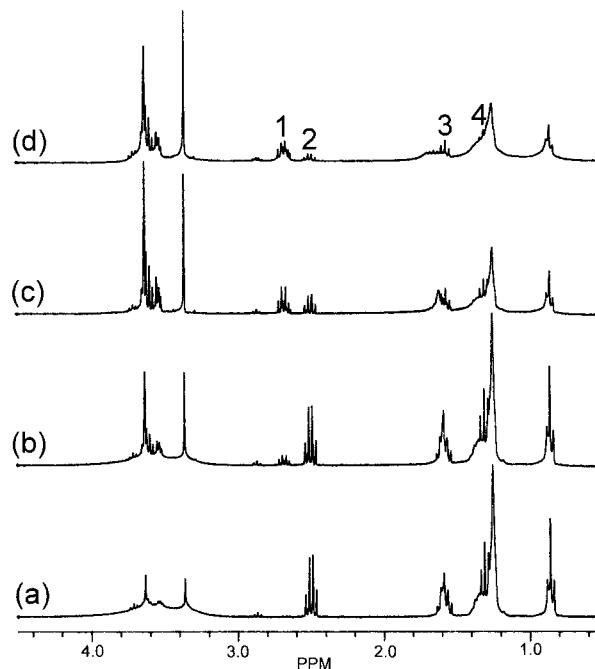
the variation in ligand size, the organic fraction of the clusters increases from AuEO<sub>2</sub> to AuEO<sub>4</sub>. It is also of interest to compare the thermal stability of these clusters with the values obtained for a series of alkanethiol-capped clusters, which are also presented in Table 1. These data show that increasing the ligand chain length results in a delayed onset of thermal decomposition, and this trend holds for the ethylene

**Table 1. Summary of TGA Results for Ethylene Oxide and Alkane-Capped Clusters**

cluster	temperature of decomposition onset (°C)	final weight %	# of atoms in thiol ligand chain
AuEO2	148	80.94	7
AuEO3	183	79.06	10
AuEO4	190	75.42	13
AuC4(1:1)	190	87.87	4
AuC6(1:1)	200	82.41	6
AuC8(1:1)	230	80.65	8
AuC12(1:1)	260	75.49	12
AuC16(1:1)	275	65.88	16

oxide clusters as well. However, when compared to alkane-capped clusters of comparable chain lengths, the ethylene oxide clusters have substantially less thermogravimetric stability. The decomposition onsets for the AuEO2, AuEO3, and AuEO4 clusters of 148, 183, and 190 °C, respectively, are significantly lower than those of the closest matching alkane clusters, with onset values of 230 and 260 °C for the AuC8(1:1)- and AuC12(1:1)-capped clusters, respectively. The previously described poly(ethylene glycol) (MW 5000)-capped cluster has a thermal mass loss temperature of 318 °C,<sup>12</sup> presumably because of its significantly longer chain length. Thermochemical stability (chemical bond breaking) correlates with thermogravimetric stability (mass loss) when the bond breaking creates molecular fragments of comparable volatility. In the case of ethylene oxide and alkane chains of comparable lengths, the volatility should be nearly equivalent or slightly lower for the ethylene oxide chain based on a comparison of vapor pressures of small-molecule analogues. Thus, for the two series of clusters in Table 1, the bonding is likely weaker for the ethylene oxide stabilized clusters. If the bond breaking is considered to occur at the gold core surface, then it is clear that the ethylene oxide structure is exerting a substantial effect on the sulfur–gold bond. It has been suggested<sup>26</sup> that the thiol–gold interaction occurs through an initial transfer of electrons from sulfur to gold, followed by loss of the proton, leading to a bond with a very small partial charge and largely covalent character. This bonding could be weakened by the presence of electronegative oxygen atoms disrupting the slight polarity of the sulfur–gold interaction and/or divalent sulfur's susceptibility to neighboring group reactivity effects.<sup>27</sup>

Once isolated, the ethylene oxide stabilized clusters retained their solubility in polar organic solvents such as  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  but became insoluble in nonpolar solvents such as heptane. In addition, the AuEO3 and AuEO4 clusters were found to be water-soluble, whereas the AuEO2 cluster is not. Interestingly, it seems the threshold of ligand length for achieving water solubility occurs between the AuEO2 and AuEO3 clusters. Aqueous solutions of the soluble clusters could be prepared under acidic (pH ~2), neutral, and basic (pH ~10) conditions, and the clusters remained stable in solution for periods ranging from days to weeks, depending on



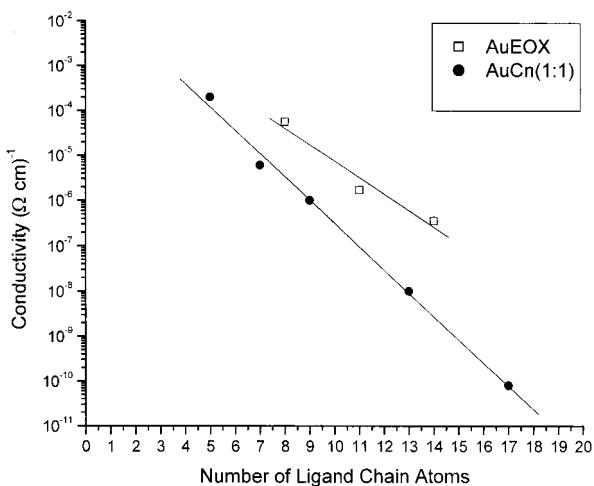
**Figure 3.** NMR exchange experiment between AuEO3 and  $\text{CH}_3(\text{CH}_2)_7\text{SH}$ : (a) initial spectrum and spectra after (b) 3 h, (c) 5 days, and (d) 20 days, where **1** is assigned to  $\text{HSCH}_2-$  from  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{SH}$ , **2** is assigned to  $\text{HSCH}_2-$  from  $\text{CH}_3(\text{CH}_2)_7\text{SH}$ , **3** is assigned to HS– from  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{SH}$ , and **4** is assigned to HS– from  $\text{CH}_3(\text{CH}_2)_7\text{SH}$ .

the pH, with no visible signs of decomposition. This stability was further examined by UV/vis spectroscopy of the AuEO3 cluster in three solutions: 1 M HCl, neutral  $\text{H}_2\text{O}$ , and 0.5 M NaOH. The acidic solution was found to be the least stable of the three, with a noticeable sharpening of the plasmon peak at 507 nm occurring after 6 h. This is indicative of an increase in the core size of the particles. After 24 h, a significant amount of black precipitate was present in the sample, and the absorbance at 507 nm had fallen to 32% of its original value, with no plasmon structure seen. After 5 days, additional precipitate had formed, and absorbance features were no longer present in the spectra. Judging from these observations, it seems probable that the acidic solution causes a loss of the stabilizing thiol ligands from the cluster surface. This results in a gradual agglomeration of the cores until their size becomes large enough that precipitation occurs. In contrast to these results, the neutral solution and the basic solution both seemed quite stable, with no sharpening of the surface plasmon peak occurring after 5 weeks at room temperature.

As mentioned previously, a water-soluble cluster based on a thiol-terminated poly(ethylene glycol) has been reported,<sup>12</sup> however, one consequence of the size of this ligand was that it prevented further exchange reactions from taking place. In the case of the ethylene oxide clusters reported here, it is still possible to carry out these reactions, as illustrated by the  $^1\text{H}$  NMR results shown in Figure 3 for the reaction of AuEO3 with octanethiol in  $\text{CDCl}_3$ . Within 3 h of mixing, the peaks associated with the AuEO3 cluster were noticeably sharper, and the quartet at  $\delta$  2.66 indicative of the  $\text{HSCH}_2-$  protons of free  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{SH}$  had begun to develop. After 5 days, substantial loss of the quartet at  $\delta$  2.51 due to the  $\text{HSCH}_2-$  protons of octanethiol was

(26) Zhong, C.; Woods, N. T.; Dawson, G. B.; Porter, M. D. *Electrochim. Commun.* **1999**, *1*, 17. (b) Krysinski, P.; Chamberlain, R. V.; Majda, M. *Langmuir* **1994**, *10*, 4286.

(27) (a) Tagaki, W. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; p 256. (b) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; p 141.



**Figure 4.** Plot showing the measured conductivity of the AuEO<sub>2</sub>, AuEO<sub>3</sub>, and AuEO<sub>4</sub> cluster series in relation to that of the AuC<sub>n</sub>(1:1) series,  $n = 4, 6, 8, 12$ , and  $16$ .

clearly evident as the octanethiol became bonded to the gold cluster surface. The octanethiol  $-SH$  triplet at  $\delta$  1.35 was also reduced in intensity during this time. These changes continued slowly and were much clearer in the spectrum taken after 20 days. In addition, a triplet developed at  $\delta$  1.56 that was attributed to the thiol proton of the  $CH_3(OCH_2CH_2)_3SH$  released from the surface of the cluster. The multiplicity of this peak and the quartet at  $\delta$  2.66 indicate that the capping group was dissociated as a thiol, not a disulfide, as suggested by previous solution observations of gold nanocluster systems.<sup>25</sup> This exchange reaction also occurs over the course of days, unlike the hours required for the synthesis of AuEO<sub>3</sub>, presumably because of the increased length of both the cluster-bound and substituting thiols.

To further characterize the ethylene oxide stabilized nanoparticles in preparation for their use as a chemical vapor sensor, the conductivity of a thin film of each cluster was measured. The results, shown in Figure 4, exhibit a clear trend of decreasing conductivity with increasing thickness of the ligand shell. This result is expected and consistent with that observed for the AuC<sub>n</sub>(1:1) analogues, also presented in Figure 4. From the figure, it is evident that the ethylene oxide stabilized clusters exhibit conductivities approximately 1 order of magnitude higher than those of the alkane clusters of corresponding atom chain length. For comparison, a similar but more pronounced trend is seen in the conductivities measured for pure poly(ethylene oxide)<sup>28</sup> and poly(ethylene),<sup>29</sup> which are  $10^{-10}$  and  $10^{-15} \Omega^{-1} \text{ cm}^{-1}$ , respectively. These polymers were chosen to approximate the conductivity that might be expected for the cluster matrix alone and offer a qualitative measure of the ability of the matrix to support electron transport.

Judging from the solubility observed for these clusters in aqueous solutions, this series of ethylene oxide stabilized clusters is of particular interest in deriving a fundamental understanding of a MIME vapor sensor's response to water vapor. Such an understanding is

critical because, in a sensor array, an element with a strong response to water vapor is very important for discriminating pattern recognition schemes. The vapor response of these devices is based on the absorption of vapors in the cluster's ligand shell and consequent modulation of electron transport between gold cores in a thin film of clusters. The magnitude of the conductance modulation is dependent on the quantity of vapor absorbed by the cluster ligand shells. An oversimplified picture of the transduction is that the vapor absorption causes a swelling of the cluster ligand shells, which increases the distance, and thereby diminishes the electron tunneling probability, between gold cores.<sup>2</sup> Such a mechanism predicts that the response to the absorption of any vapor would be a conductance decrease. Although such a decrease is observed in many examples involving nonpolar vapors, there are important examples such as water and alcohol vapor exposures where the conductance increases.<sup>2,30</sup> This conductance increase usually correlates with responses to vapors with very polar chemical structures. For the general purpose of enhancing selectivity of the MIME sensor and the particular purpose of obtaining a cluster with a uniquely strong response to water vapor, we have previously followed the approach of introducing terminal functional groups onto the alkanethiol ligand molecule.<sup>30</sup> Although interesting responses to vapors of varying polarity have been observed, this approach has not yet resulted in a good understanding of the correlation between the vapor response and the cluster ligand structure, nor has it resulted in a strongly water vapor responsive cluster. The ethylene oxide stabilized clusters described here differ in that they contain a capping group in which the entire chain of the thiol ligand molecule is hydrophilic (and nonionic). The systematic variation in structure of these clusters could serve as a tool for obtaining an understanding of complexities associated with polar structures in the vapor-response mechanism.

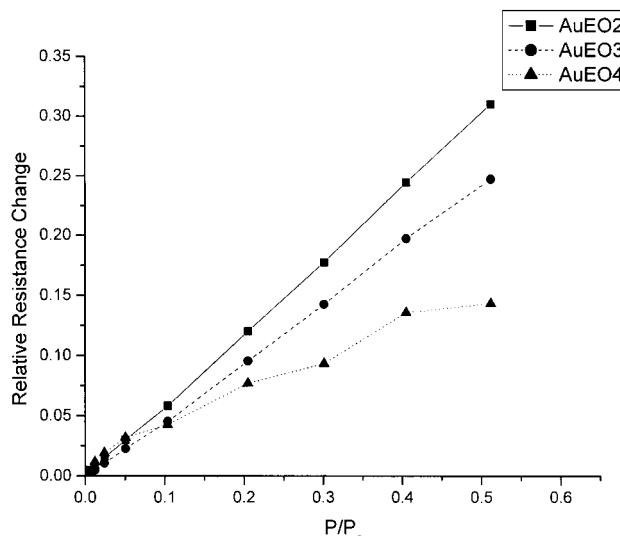
As in previous work utilizing the alkanethiol-stabilized cluster, the set of vapors studied includes toluene, 1-propanol, and water.<sup>2</sup> This selection provides for a large variation in polarity, while at the same time, the very similar vapor pressures of the three compounds allow for a more direct comparison of the chemical selectivity afforded by the nanocluster film. The matching of the vapor pressure of the analytes is important because vapor pressure is a strong determinant of vapor partitioning at an air–solid interface, and vapor-pressure-derived effects will superimpose on any selective effects of chemical interactions between the vapor and the nanocluster film.

The vapor-response isotherms for the AuEO<sub>2</sub>, AuEO<sub>3</sub>, and AuEO<sub>4</sub> clusters in the MIME sensor configuration exposed to vapors of toluene, 1-propanol, and water can be found in Figures 5–7, respectively. These data were obtained from measurements of the conductance changes occurring during purge/exposure cycles for each vapor. Vapor concentrations were varied by dry air dilution of the effluent from 15 °C bubblers and are expressed as dilution factors ( $P/P_0$ ) that range from 0.50 to 0.0001, corresponding to the range from 8000 to 1.6 ppmv,

(28) Bailey, F. E.; Koleske, J. V. *Poly(Ethylene Oxide)*; Academic Press: New York, 1976; pp 140–141.

(29) Raff, R. A. V.; Allison, J. B. *Polyethylene*; Interscience Publishers: New York, 1956; pp 328–331.

(30) Snow, A. W.; Wohltjen, H. U.S. Patent 6,221,673, 2001.



**Figure 5.** Toluene isotherm data for the AuEO2, AuEO3, and AuEO4 cluster series.

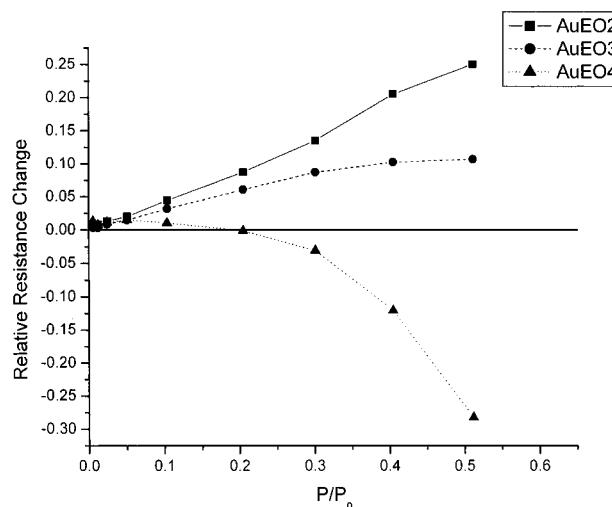
respectively.<sup>31</sup> The relative resistance is the change in resistance caused by the vapor exposure normalized to the baseline resistance of the MIME device under purge conditions.

All of the isotherms for the toluene response (Figure 5) display an increase in resistance with toluene vapor concentration, and in the case of the AuEO2 and AuEO3 clusters, the response is linear. This behavior is consistent with the aforementioned swelling mechanism. The AuEO4 isotherm displays a diminished response at the high end of the isotherm. The order of response or sensitivity ranking is AuEO2 > AuEO3 > AuEO4. This order parallels the aqueous solubility observations and appears to indicate that the cluster with the shorter ethylene oxide chain is more compatible with a nonpolar organic medium. However, it should be noted that this response is less than half that of an alkanethiol-stabilized cluster to toluene.<sup>2</sup>

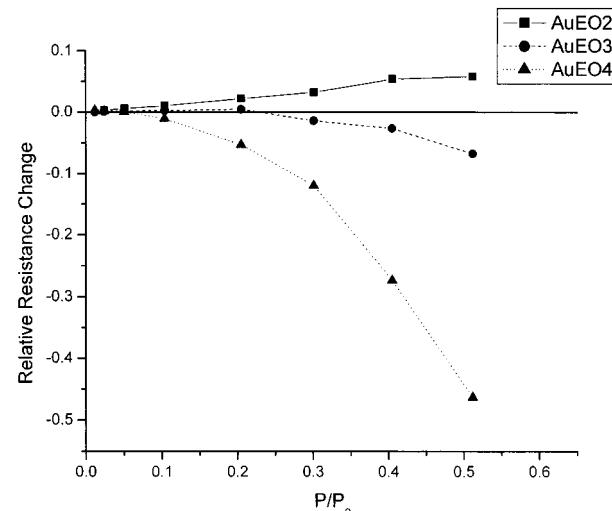
The isotherms for the 1-propanol response (Figure 6) are weaker and more complex. The response of the AuEO2 cluster displays a continuous resistance increase, whereas that for the AuEO3 cluster levels off at the high-concentration end of the isotherm. The AuEO4 cluster isotherm displays a crossover from a very modest resistance increase to a strong resistance decrease. This appears to indicate that at least two different mechanisms of transduction are operating. Clearly, the swelling mechanism is being overridden by another mechanism that causes the resistance decrease.

The isotherms for water vapor (Figure 7) display responses that are even further shifted in the direction of decreasing resistance. For the AuEO4 cluster, it appears that the mechanism that results in a resistance decrease upon absorption of water vapor dominates over the swelling mechanism. The AuEO3 cluster initially has a very weak resistance increase, followed by a crossover to a resistance decrease. The hydrophobic AuEO2 cluster maintains a weak response in the direction of increasing resistance.

(31) These vapor concentrations are calculated from an average 15 °C vapor pressure (13.3 mm) for the set of toluene (16.6 mm), 1-propanol (10.5 mm), and water (12.8 mm) 15 °C vapors.



**Figure 6.** 1-Propanol isotherm data for the AuEO2, AuEO3, and AuEO4 cluster series.



**Figure 7.** Water isotherm data for the AuEO2, AuEO3, and AuEO4 cluster series.

From these results, it appears that the hydrophilic character of the cluster increases with increasing length of the ethylene oxide chain in the ligand shell. As the vapor also becomes more hydrophilic, the dominant transduction mechanism changes from one that results in increasing resistance to one that causes decreasing resistance. It appears that the combination of a hydrophilic ligand shell and an adsorbed polar vapor promote an electron transport between cluster cores that more than compensates for any increase in core separation distance caused by swelling of the ligand shell. Although a full understanding of the electrical conductivities and vapor sensitivities of this series of ethylene oxide stabilized clusters is beyond the scope of this paper, our results show that a correlation exists between the conductivity and the polar character of the shell and/or the adsorbed vapor. Clearly, the insulating barrier between clusters is being modulated by the presence of dipoles in this regime. Mechanisms that can result in such behavior have been described<sup>32</sup> and involve electron transport either through or over the energy barrier.

(32) Fishelson, N.; Shkrob, I.; Lev, O.; Gun, J.; Modestov, A. D. *Langmuir* **2001**, *17*, 403.

In both cases, this energy barrier is affected by the polarizability of the medium between the metal nanoparticles. Future work will be required to clarify the details of this transport and especially the role of the dielectric.

Overall, the ethylene oxide stabilized clusters described above combine several very attractive features. They are water-soluble, charge-neutral, and high in purity, and they retain the ability to undergo thiol substitution reactions. This fact has important implications for their potential incorporation into nanoelectronics through self-assembly operations. In addition, we have successfully used these clusters in a MIME sensor

format and demonstrated their strong response to water vapor exposure. Of considerable interest is the potential of these clusters to participate in self-assembly operations under aqueous conditions, and studies to examine this possibility are currently underway.

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